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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Suspension Polymerization Process

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of vinyl polymers and more particularly to improved methods for the suspension polymerization of vinyl monomers to obtain superior polymeric products.

Vinyl polymers, and particularly those obtained from vinyl aryl monomers such as styrene, are commonly prepared in bead or "pearl" form by processes in which the monomer is dispersed in a liquid medium, usually water, which is a non-solvent for the monomer, polymerization taking place within the suspended globules or droplets. Referred to as suspension polymerization methods, such procedures have the advantage of offering superior control of temperature, polymerization rate, and molecular weight of the polymer. However, the suspension polymerization methods have one major drawback, arising because the material being polymerized passes through a sticky, viscous phase during which the particles tend to coalesce or cling together, causing formation of aggregates with resultant lack of uniformity as to particle size and molecular weight of the product. Various ways have been proposed for combating this problem, the most practical and economical approach being to add to the initial monomer suspension various types of suspension aids.

The suspension aids most frequently proposed heretofore have been relatively insoluble inorganic suspension stabilizing agents such as tricalcium phosphate, in finely par-

ticulate form, such agents providing a physical barrier between the monomeric or partially polymerized droplets and thus tending to prevent agglomeration. Various protective colloids, emulsifiers and surface active agents have also been proposed in the past. In all, however, no way has heretofore been found for so protecting the suspension and controlling the polymerization that polymers of desired high molecular weight and relatively large but controlled particle size can be obtained.

Control of the size of the beads or particles of the polymer product is of particular importance, particularly when, as in the production of certain polystyrenes, the product is made foamable and is to be used for the production of insulating board by continuous extrusion. Thus, it is highly desirable to obtain polystyrene in a bead size range of 590—2000 microns, with a viscosity average molecular weight in excess of 225,000 and a shrinking temperature of at least 110°C. Such a product has not been attainable heretofore by any method suitable for practical commercial application.

The invention is based on the discovery that, in the suspension polymerization of vinyl monomers, these difficulties can be largely or completely overcome by employing the combination of a particular inorganic suspension stabilizing agent, a surface active agent which is either an anionic agent or an amphoteric agent having both carboxyl and amino functional groups, and a protective colloid, the three suspension aids being incorporated in the initial monomer suspension in particular proportions (hereinafter described), and then accomplishing polymerization with agitation and heat.

According to the present invention there is provided a process for suspension polymerization of vinyl monomers which comprises in-

corporating in an aqueous vinyl monomer suspension 1) a thixotropic paste of one or more inorganic finely particulate suspension stabilizing agents having an average particle size of 0.5 micron and water in a weight ratio of solid to water of from 1:2 to 2:1, the total weight of stabilizing agent being 0.1 to 2% by weight of the monomer, 2) one or more surface active agents selected from anionic agents or amphoteric surface active agents having both carboxyl and amino functional groups in a total amount of 0.01 to 2% by weight of the suspension, and 3) a protective colloid in an amount of 0.0001 to 0.005% by weight of the suspension, and heating the mixture to effect polymerization.

The inorganic suspension stabilizing agent is employed in the form of a thixotropic paste the particles of which have an average size of 0.5 micron, the paste usually being produced by working the inorganic compound with water in a colloid mill, the inorganic compound initially having an average particle size of 0.5 micron and the operation of the colloid mill being such as to accomplish through dispersion of the solid particles without extensive particle size reduction. The thixotropic paste must have a solids-to-water ratio of 1:2—2:1, a weight ratio of approximately 1:1 being most advantageous. The inorganic compound employed must be insoluble or, substantially insoluble in the suspension medium. Thus, any substantially insoluble phosphate of calcium, barium boron, strontium, magnesium, aluminum, zinc or cadmium can be employed. Other typically suitable compounds include the aluminum silicates and fluoro-silicates, magnesium carbonate, magnesium oxide, talc (hydrous magnesium silicate), barium oxalate, barium sulfate, and calcium carbonate. Such agents can be used singly, or the thixotropic paste can employ a combination of different agents such, for example, as tricalcium phosphate with a lesser proportion of calcium carbonate. Compounds of copper or iron are to be avoided.

The thixotropic paste is employed in a proportion providing an amount of suspension stabilizing agent or agents equal to 0.1—2.00% of the total weight of vinyl monomer employed. Advantageously, an amount of suspension stabilizing agent or agents equal to 0.25—0.75% of the monomer weight can be employed.

As surface active agents employed in accordance with the invention, the anionic agents are particularly effective. Typically, we can employ sodium beta naphthalene sulfonate, sodium nonyl naphthalene sulfonate, or sodium butyl naphthalene sulfonate. As amphoteric surface active agents containing both carboxylic and amino groups, such compounds as the partial sodium salt of N-lauryl

imino dipropionic acid or N-lauryl amino propionic acid are typical.

The surface active agent, or a combination of such agents, is employed in an amount equal to 0.01—2.00% by weight of the total suspension, the narrower range of 0.06—1.20% being most advantageous.

The protective colloid can be a salt of a polyacrylic acid, a gelatin, pectin, any of the suitable starches, the alginates, carboxymethyl cellulose and equivalent cellulose derivatives, polyvinylpyrrolidone. Particularly good results are achieved with sodium polyacrylate. The protective colloid is employed in an amount equal to 0.0001—0.005% of the total suspension weight, the narrower range of 0.0001—0.0017% being superior.

The improvements attained by the invention depend not only upon the use of the three suspension aids discussed above but also on the nature and manner of introduction of the inorganic compound employed as the suspension stabilizing agent. The desired results cannot be obtained under practical operating conditions if the inorganic suspension stabilizing agent is not introduced in the form of a thixotropic paste. In the suspension, the fine particles of the inorganic compound intervene physically between the droplets of monomer and prevent the droplets from directly engaging each other and coalescing. To be capable of acting effectively in this manner, the inorganic compound must have a particle size which is small as compared to the size of the droplets, and the inorganic particles must be uniformly dispersed throughout the suspension. Further, such uniform dispersion must persist throughout at least most of the polymerization procedure.

We have found that, if the inorganic suspension stabilizing agent is added as a dry material to the suspension, successful polymerization to produce a polymer of uniform relatively large bead or particle size cannot be assured even if the amount of suspension stabilizing agent is increased to several times the proportions hereinbefore recited. Further, we have determined that the reason for this difficulty is that, even though the inorganic compound is employed with an average particle size of about 0.5 micron, a uniform dispersion in the aqueous medium of the suspension cannot be achieved under practical conditions. This can be demonstrated on a comparative basis by the procedure of the following experiment:

#### EXPERIMENT 1

A quantity of technical grade tricalcium phosphate is divided into two equal portions, the average particle size in each case being 0.5 microns. One such portion is combined with an equal weight of water and subjected to the action of a colloid mill until

a thixotropic paste is employed, the colloid mill being set so as not to accomplish substantial grinding of the particles. The other portion of tricalcium phosphate is employed dry.

5 Equal quantities of water are introduced into separate glass containers each equipped with a motorized rotary agitator. The thixotropic paste is added to one container and the dry quantity of tricalcium phosphate to the other, the amounts of water employed being such that the weight of tricalcium phosphate is equal to 0.5% of the weight of the water in each container. High speed agitation is carried out for 1 hour and the two containers are then allowed to stand for an additional hour without agitation, the containers then being observed for any tricalcium phosphate which has settled to the bottom. In the container to which the thixotropic paste was added, only a small amount of a very fine sediment will be observed. In the container to which the dry tricalcium phosphate was added, a distinctly larger quantity of settled tricalcium phosphate will be found, this quantity including not just fine particles but relatively large agglomerates of tricalcium phosphate which were not dispersed by the high speed agitation. In actual polymerization runs under various typical conditions, it has been found that any significant agglomeration of the inorganic suspension stabilizing agent in the suspension before completion of the viscous, sticky intermediate stage of the polymer will lead at least to non-uniformity of bead or particle size in the finished polymer and frequently to total failure of the suspension, with loss of the entire run.

Though achieving of a dependable uniform dispersion of the inorganic stabilizing agent is an essential prerequisite, this factor alone will not provide success in producing polymer beads of the desired uniform relatively large size and high molecular weight. Though both the inorganic compound, such as tricalcium phosphate, and a surface active agent, such as sodium beta naphthalene sulfonate, contribute to establishing a good suspension and preserving the same throughout the critical stages of polymerization, both such agents, when employed in increasing proportions, tend to cause the bead or particle size of the product to decrease, as demonstrated by the following experiments.

#### 55 EXPERIMENT 2

A thixotropic paste was produced by combining 8 parts by weight technical grade tricalcium phosphate (average particle size 0.5 micron) and 12 parts by weight demineralized water and passing the mixture twice through a colloid mill. The resulting paste was combined with 1090 parts of demineralized water in a 3 litre glass reactor equipped with a motorized rotary agitator operated at 400

r.p.m. 1100 parts by weight of styrene monomer was then added slowly. The suspension was then heated to 25–30°C., and 1.1 parts by weight of azo bisisobutyronitrile, 0.55 parts of benzoyl peroxide and 0.55 parts of tertiary butyl peroxide were added. Polymerization was accomplished with the reactor sealed, by heating to 80°C. in 1 hour, holding at 80°C. for 6 hours, heating to 87°C. in 1 hour, holding at that temperature for 6 hours, heating to 95°C. in 1 hour, and holding at 95°C. for 3 hours. The suspension was cooled, acidified to pH 1 with dilute hydrochloric acid, and the beads recovered, washed, and dried at 70°C. for 5 hours. The procedure was repeated 5 times with a different proportion of sodium beta naphthalene sulfonate incorporated at the time of addition of the tricalcium phosphate in each run, the particle size of the product for each run being shown by the following tabulation:

Run	Sodium beta naphthalene sulfonate (% by wt.)	Percent of polymer product larger than 590 microns	
1	0.068	51.0	90
2	0.248	21.8	
3	0.338	14.5	
4	0.430	13.0	
5	0.584	3.4	

#### EXPERIMENT 3

The procedure of Experiment 2 was repeated 5 times, but with the sodium beta naphthalene sulfonate constant at 0.45% by weight and the proportion of tricalcium phosphate varied; the results as to particle size being tabulated as follows:

Run	Tricalcium phosphate (% of monomer wt.)	Percent of polymer product larger than 590 microns	
6	0.364	77.8	105
7	0.545	67.1	
8	0.730	13.0	
9	0.910	26.2	
10	1.090	7.8	110

On the other hand, we have found that the particle size of the polymer can be increased, while still retaining effective proportions of the inorganic suspending agent and surface active agent, by incorporating a protective colloid as a third suspension aid. The following Examples illustrate the invention.

#### EXAMPLE 1

The procedure of Experiment 2 was repeated 5 times, employing an amount of tricalcium phosphate equal to 0.73% of the weight of styrene monomer, and sodium beta naphthalene sulfonate equal to 0.45% of the total weight of the suspension; but introduc-

ing a different amount of sodium polyacrylate into the suspension for each run. In each run, the surface active agent and the protective colloid were added after the catalysts had been introduced and the suspension had been heated to 40°C., the sodium polyacrylate being added as a 15% aqueous solution. The results as to polymer bead size are tabulated below:

Run	Sodium polyacrylate (% by wt.)	Percent of polymer product larger than 590 microns
11	0.000169	17.8
12	0.000337	10.0
13	0.000673	33.8
14	0.001005	72.0
15	0.001340	85.2

The foregoing runs are typical for small scale laboratory runs employed to determine the effect of such variables as relative proportions. The following example is representative for runs carried out under conditions more closely approximating commercial production runs.

#### EXAMPLE 2

A 10-gallon glass-lined reaction vessel was employed, equipped with a propeller agitator driven at 260 r.p.m. for all runs. All runs were carried out under an inert nitrogen atmosphere, and with the total charge equal to about 80% of reactor capacity. For each run, the following formulation was employed:

Ingredient	Weight in lbs.
Styrene monomer	33.2
Demineralized water	33.2
Azobisisobutyronitrile	0.0244
Benzoyl peroxide	0.0121
Tertiary butylperbenzoate	0.0298
Sodium polyacrylate (1% aqueous solution)	0.77
Tricalcium phosphate	as tabulated below
Sodium beta naphthalene sulfonate	as tabulated below

In each run, the tricalcium phosphate was added in the form of a homogenized thixotropic paste prepared as in Experiment 2, the paste being added to the water before addition of the styrene monomer. In each run, the sodium polyacrylate and sodium beta naphthalene sulfonate were added after the catalysts had been introduced and the suspension heated to 40°C. Polymerization was accomplished in each run by heating to 85°C. in 45 minutes, holding at 85°C. for 5 hours, heating to 100°C. in 30 minutes, holding at 100°C. for 4.5 hours, heating to 130°C. in 2 hours, and holding at 100°C. for 4.5 hours. The suspension was then acidified to pH 1 by addition of dilute hydrochloric acid, and the beads recovered, washed and dried in air at 70°C. for 5 hours. The results as to bead size for the polymer are tabulated below:

Run	Tricalcium phosphate (% of monomer wt.)	Sodium beta naphthalene sulfonate (% by wt.)	Percent of product larger than 590 microns
16	0.650	0.502	88.9
17	0.585	0.475	91.1
18	0.510	0.410	93.5
19	0.364	0.292	99.2
20	0.328	0.264	100.0

For each run, the polymer had a viscosity average molecular weight of more than 225,000 and a shrink temperature more than 110°C.

When "shrink temperatures" are mentioned in the foregoing examples, the shrink temperature is obtained by foaming a sample of the beads by heating them in boiling water for 3 minutes, then recovering the foamed beads and determining their bulk density, then dividing the foamed beads into separate samples and heating each such sample at a different selected temperature in the range of 100—130°C. in an air oven for 30 minutes. Thereafter, the beads are cooled in air to room temperature and the bulk density again determined. The shrink temperature is that temperature at which an appreciable change in bulk density of the foamed beads is observed. For example, if the separate samples are heated to 100°, 105°, 110°, 115°C., respectively, and no change in bulk density is observed in the samples heated to 110°C. or less, but a significant change is noted in the sample heated to 115°C., the shrink temperature is taken as 110—115°C.

#### WHAT WE CLAIM IS:—

1. A process for suspension polymerization of vinyl monomers which comprises incorporating in an aqueous vinyl monomer suspension 1) a thixotropic paste of one or more

- inorganic finely particulate suspension stabilizing agents having an average particle size of 0.5 microns and water in a weight ratio of solid to water of from 1:2 to 2:1, the total weight of stabilizing agent being 0.1 to 2% by weight of the monomer, 2) one or more surface active agents selected from anionic agents or amphoteric surface active agents having both carboxyl and amino functional groups, in a total amount of 0.01 to 2% by weight of the suspension, and 3) a protective colloid in an amount of 0.0001 to 0.005% by weight of the suspension, and heating the mixture to effect polymerization.
- 5 2. A process according to claim 1 wherein the weight ratio of stabilizing agent to water in the thixotropic paste is 1:1.
- 10 3. A process according to claim 1 or claim 2 wherein the stabilizing agent is tricalcium phosphate.
- 15 4. A process according to claim 1 or claim 2 wherein tricalcium phosphate with a lesser proportion by weight of calcium carbonate is used as the stabilizing agents.
- 20 5. A process according to claim 1 or claim 2 wherein the stabilizing agent is one or more of the phosphates of calcium, barium, boron, strontium, magnesium, aluminum, zinc, or cadmium, an aluminum silicate or fluorosilicate, magnesium carbonate, magnesium oxide, hydrous magnesium silicate, barium oxalate, barium sulfate or calcium carbonate.
- 25 6. A process according to any one of claims 1 to 5 wherein the amount of stabilizing agent is 0.25 to 0.75 per cent by weight of the monomer.
- 30 7. A process according to any one of claims 1 to 6 wherein the surface active agent is used in an amount of 0.06 to 1.2 per cent of the total weight of the suspension.
- 35 8. A process according to any one of claims 1 to 7 wherein the anionic surface active agent is sodium beta naphthalene sulfonate, sodium nonyl naphthalene sulfonate or sodium butyl naphthalene sulfonate.
- 40 9. A process according to any one of claims 1 to 8 wherein the amphoteric surface active agent is the partial sodium salt of N-lauryl imino dipropionic acid or N-lauryl amino propionic acid.
- 45 10. A process according to any one of claims 1 to 9 wherein the protective colloid is used in an amount of 0.0001 to 0.0017 per cent of the total weight of the suspension.
- 50 11. A process according to any one of claims 1 to 10 wherein the protective colloid is a salt of a polyacrylic acid.
- 55 12. A process according to claim 11 wherein the salt of the polyacrylic acid is sodium polyacrylate.
- 60 13. A process according to any one of the preceding claims wherein the vinyl monomer is styrene.
- 65 14. A process for the suspension polymerization of vinyl monomers according to claim 1 substantially as described in either one of the specific Examples.
- 70 15. Vinyl polymers whenever produced by the process claimed in any one of the preceding claims.
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